Freeze desalination as point of use water treatment technology: A case of chromium (VI) removal from water

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Abstract

Options to develop tanning industries could be hindered even in the presence of huge leather industry raw materials due to the requirements of high-tech contaminant removal technologies, especially in developing countries. This study was initiated to investigate the efficiency of freeze desalination for Cr(VI) removal using refrigerators to generate fresh water. Synthetic solutions that represent major ion compositions of drinking water as well as deionized water to which known concentrations of Cr(VI) spiked into it, were added and frozen in a closed freezer unit. The effects of different parameters such as initial concentration, freeze duration, ice nucleation, fraction of ice volume, and influence of co-occurring ions were evaluated in relation to the quality of produced ice. The physicochemical characteristics of the produced meltwater were also evaluated. A high total water recovery of up to 85% was achieved in the experimental evaluation. Cr(VI) removal efficiency of up to 80% from simulated tap and 93 to 97% for deionized water spiked with Cr(VI) were found in this batch partial freezing. Freeze desalination was found to be relatively viable desalination technology in terms of quality of water produced, options on the use of cost effective refrigerants and technologies which could have a pertinent importance to save energy consumption of freezers.

Keywords: Ice nucleation, Freeze desalination, Refrigerator, Refrigerant, Progressive freezing

1. Introduction

Chromium is one the priority pollutants list under clean water act of US EPA which can be introduced into natural waters due to the discharge of a variety of industrial wastewaters containing Cr. Wastewater generated by leather tanning, electroplating, textile, and metal finishing industries are among the major contributing sources. Uncontrolled solid and liquid waste discharges into open water systems from domestic use and industries with minimal or no treatment are common in developing countries (Tamiru 2006). Among the various tanning methods, more than 90% of the leathers tanned globally, contain chromium, with 30–50% of the Cr used in the process leaching into the environment (Mannucci et al. 2010). According to the Black Smith institute report (2007), various drinking water sources in developing countries are highly polluted with Cr(VI). In Ethiopia, literatures are indicating the presence of hexavalent chromium in surface waters such as streams and rivers nearby leather industries (Mengistie et al. 2016) which have been shown to exceed, 0.05 mg/L, the maximum permissible level for drinking water set by the WHO (WHO 2011; Dsikowitzky et al. 2013).

Chromium exists in different valence states. Cr(VI) and Cr(III) are common in the natural environment, with Cr(VI) being more mobile and toxic than Cr(III). Cr(VI) is relatively mobile in the environment and due to its powerful oxidizing nature, it is even evidenced as being mutagenic and carcinogenic (Witt et al. 2013). Alternatively, Cr(III) is important to maintain balanced glucose metabolism in mammals (Kotaś and Stasicka 2000). The existence of Cr in different oxidation states has a significant consequence on the transport and the fate of Cr species, varying in their treatment capabilities and costs (Stanin 2005). Considerable efforts, therefore, have been made to treat mostly Cr(VI) containing water/ wastewater.

Widely employed methods for Cr(VI) removal include chemical precipitation (primarily by reducing Cr(VI) to Cr(III)), ion exchange, electrodialysis, reverse osmosis, and adsorption (Rengaraj, Yeon, and Moon 2001; Gheju and Balcu 2011; Shi, Zhang, and Chen 2011; Yari et al. 2013). Sludge production, cost unaffordability, and unpleasant tests are among the challenges encountered for most of the methods especially in developing countries. The main drawbacks for membrane separation processes, however, are clogging, adsorption and cake layer formation on the membrane by the pollutants. Especially, the high organic content of tannery effluents leads to rapid scaling and biofouling of RO membranes with a consequent reduction in flux rates and performance. Thermal processes which involve phase changes, such as membrane distillation and freezing processes, are employed frequently (Das et al. 2006; Scheumann & Kraume 2009; Mahdavi et al. 2011). However, such treatments are handicapped by high treatment cost. Treating industrial wastewater by segregation of waste streams is a very important step in tannery pollution prevention although it is not widely applied (Lofrano et al. 2013). Moreover, it is often not feasible to apply high-tech membrane-based solutions in semi-urban and rural areas of developing countries.

Freezing-melting with subsequent removal of contaminants is an alternative physical process which can be used for desalting, based on the different freezing points of fresh and salt waters. It has been reported as being effective to remove various organic and inorganic impurities from water/wastewater (Lemmer et al. 2001; Gao and Shao 2009). When freeze concentration is used to purify water or liquid waste, impurities are separated from the ice phase during formation of the ice crystals. Two basic freeze desalination methods are available: suspension and progressive freeze crystallization. In both processes, inclusion of most compounds in the ice crystal lattice is impossible due to the small dimensions of ice crystal lattice. In progressive freeze crystallization, the separation of ice crystals formed from the concentrated mother liquor is much easier than in the conventional suspension crystallization, in which many small ice crystals are formed (Lu and Xu 2010; Mahdavi et al. 2011). In the current study, we focused on assessing the potential of home-use refrigerators to generate Cr(VI) free water.

2 Materials and methods

2.1 Reagents

A 1000 mg/L Cr(VI) were prepared from potassium dichromate (Riedel-de Haen, Germany) in double-distilled water. Working solutions were prepared by diluting Cr(VI) stock solutions. 1000 mg/L Cr(VI) standards of analytical grade were employed for calibration. Series of standard solutions were prepared by pipetting suitable volumes of Cr(VI) solution (5 mg/L) using a Thermo Scientific FJ40512 Finnpipette. Fresh solutions were prepared prior to each experiment. Moreover, simulated tap water containing major ions (Ca^{2+} 58.64 mg/L, Mg^{2+} 29.26 mg/L, Na^{+} 92.67 mg/L, K^{+} 20 mg/L, HCO_3^{-} 470 mg/L, and SO_4^{2-} 60 mg/L) spiked with 5 mg/L of Cr(VI) was prepared and tested.

2.2. Experimental setup

Prior to starting the experiment, smooth plastic containers of 250 mL capacity were selected. Thus, smooth containers are required to avoid inclusion of contaminants in ice crystals due to the roughness of surfaces involved, which may cause serious contamination during ice crystal formation. The influence of surface roughness of containers involved was previously described (Williams et al. 2015). Concentrations variations were studied in the range of 1 to 300 mg/L. To reject the concentrated Cr(V), a plastic tube of ca. 20 mm diameter was inserted with its upside down in each plastic beaker (**Fig. 1**). After each different partial freezing steps (freezing until 85%

meltwater remained), three beakers were taken from the freezer and ice crystals were separated from the remaining water by rejecting liquid part. The whole procedure was repeated after different time intervals until only a small volume of concentrated solution remained. To desorb Cr(VI) weakly adsorbed to the surface of the ice, the surface was washed three times by rinsing with small cold deionized water at 5 ^{o}C. Subsequently, the ice crystals were melted letting to room temperature and analyzed for Cr content using a colorimetric method. Thus, 250 mg chelating agent, 1,5-Diphenylcarbazide (BDH, England), was dissolved in 50 mL acetone (Himedia, India) and stored in an amber bottle. The pH of sample solutions was adjusted to 2.0 ± 0.5 using 0.5 M sulfuric acid. Then, 2 mL of the diphenylcarbazide solution was added to each sample (100 mL) and the mixture was allowed to stand for 10 min. to obtain full color development. Absorbance was measured at 540 nm using a Janway 6051 colorimeter. Background correction was performed by analyzing blanks. Calcium, magnesium, potassium and sodium concentrations were measured in the melted ice using an inductively coupled plasma optical emission spectrometer (VISTA-MPX CCD Simultaneous Varian version 2.0). Conductivity and solution pH were measured using a microprocessor conductivity meter (WTW LF 537) and a digital pH meter ORION star A211, respectively.

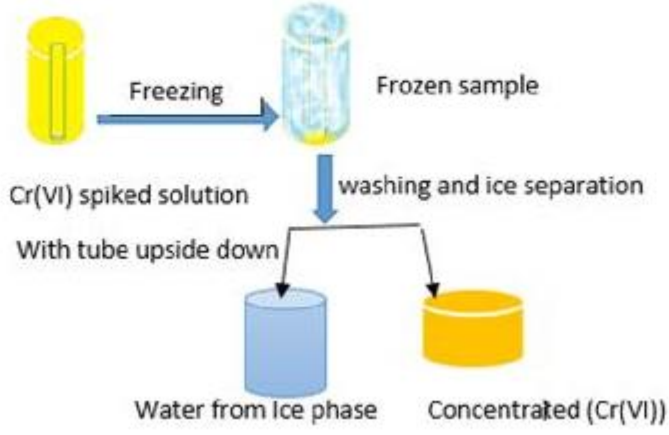

Fig. 1. Overview of the experimental setup with ca. 20 mm diameter plastic tubes being inserted upside down in plastic beakers containing Cr(VI) contaminated water.

The performance of the freeze separation process was expressed using the following parameter:

The efficiency of freeze separation (E) was evaluated through eq. (1).

$$E=(1-Cs*Vs/Co*Vo)*100 \quad (1)$$

Where E is the efficiency of freeze separation, V_O initial volume of Cr(VI)-containing solution/simulated water, V_S volume of the solid phase (ice) after melting (mL), C_o initial concentration of fluoride in solution/simulated water (mg/L) and C_S concentration of fluoride in ice phase (mg/L).

3 Results and discussion

3.1 Deionized water spiked with Cr(VI)

It was presented in Fig. 2 that, the removal of Cr(VI) from aqueous solutions of 5 mg/L Cr(VI) as function of freeze duration and fraction of water transformed into ice was illustrated. It could be concluded that initially the removal percentage increased up to nearly 97% as the freezing time and volume of ice increased. Afterwards, the entrapment of Cr(VI) in the ice phase increased and the removal percentage started decreasing. Such trend has been observed also for the removal of other soluble organic pollutants (Lorain et al. 2001). It was shown in literature that, as the residual liquid volume got too small, the removal efficiency decreased, due to the impossibility to maintain regular contact between the liquid and solid phases (Zhang et al. 2016). Long freeze duration results an entrained of impurities/ions into ice crystals, relative to the volume of the solution, because the concentrated ions builds up an interface and tends to inclusions afterwards (Chang et al. 2016). That is, as the volume of liquid water remains relatively small, the solid/liquid interface became more labile and ice crystal forms dendrites with more advanced ice branches gradually (Yang et al. 2017).

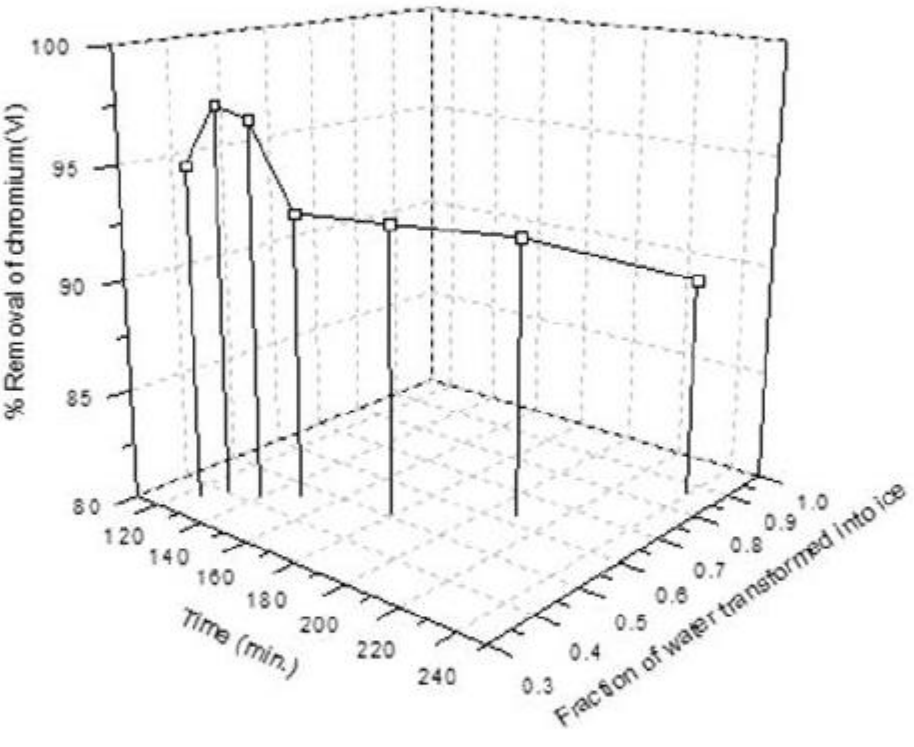

Fig. 2. Relation between the fraction of water transformed into ice (V/V), percent Cr(VI) removed and freeze duration (conditions: deionized water with spiked Cr(VI) at initial concentration of 5 mg/L & freeze temperature of 249.15 K, initial volume 250 mL)

Experimental data and literature search results have shown that the surface roughness plays a very crucial role in ice nucleation. A preliminary experiment illustrated that the use of rough surface plastics resulted enhanced inclusion of Cr(VI) into the ice crystals. The impact of surface roughness on the freeze delay time was previously described (Hao et al. 2014). The effective partition constant (K) in between the ice and liquid phases can be defined according to literature (Liu, Miyawaki, and Nakamura 1997).

$$K = C_S/C_L \quad (2)$$

Where C_S [wt%] and C_L [wt%] are chromium concentrations in ice and solution phases, respectively. The value of K is situated between 0 & 1, revealing meanings of no salts in solid phase and no freeze concentration, respectively. In observation of the mass balance, a small volume increase in the ice phase results in a small decrement of the volume of the solution phase ($-dV_L$), whereas the concentration of the solute increases in the solution phase by dC_L. Assuming complete mixing in the solution phase and no mixing in the ice phase, the mass balance of solutes can be presented as follows (Liu, Miyawaki, and Nakamura 1997):

$$C_L V_L = - Cs\, dV_L + (C_L + dC_L)(V_L + dV_L) \quad (3)$$

By substituting Eq. (2) in Eq. (3):

$$(dC_L + C_L/ C_L)/(dV_L/ V_L) = K - 1 \quad (4)$$

Integrating Eq. (4):

$$(1- K)\log(V_L/ Vo) = 1og(Co/ C_L) \quad (5)$$

Where Co [wt%] is the initial concentration of chromium (VI) before freezing, C_L [wt%] is the concentration of concentrate, and Vo is the initial volume used. Fig. 3 shows a linear plot of experimental data used to calculate the effective partition constant, K, for the progressive freeze desalination of aqueous solution spiked with 5 mg/L Cr(VI). Using Eq. (5), K-value of 0.064 was obtained from the slope of the linear plot, which indicates the effectiveness of the progressive freeze concentration process. It is known that, in any cases, the lower K value shows higher efficiency of the system.

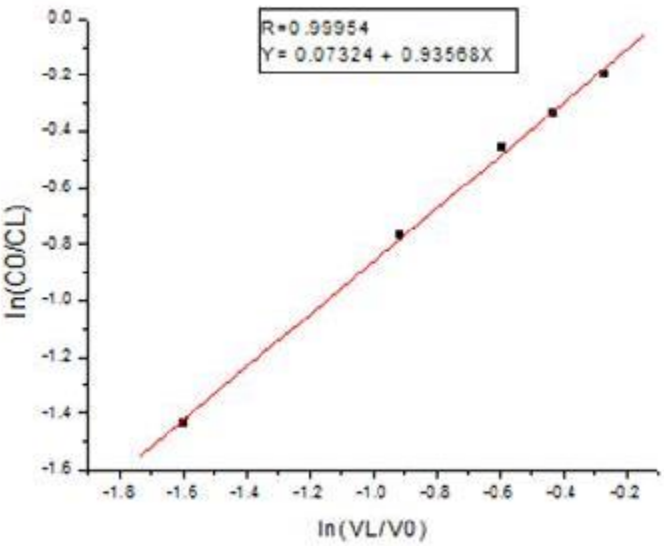

Fig. 3. Relationship between Co/C_L and V_L/Vo when subjecting 5 mg/L Cr(VI) in deionized water to freeze desalination at a temperature of 249.15 K.

3.2 Removal of Cr(VI) from simulated tap water

Drinking water contains several substances that can affect the particular ion removal/ water purification process. The removal of Cr (VI) from simulated water and aqueous solutions has been illustrated in Fig. 4. The influence of presence of some dissolved ions with Cr(VI) removal by freeze desalination was also investigated. In the simulated tap water, as presented in Table 1, the Cr(VI) removal efficiency was lower as compared to the removal efficiency in deionized water spiked with Cr(VI). In case of tap water, TDS played an inverse role in the Cr(V) removal efficiency. The effect of common ions existing in drinking water and inverse relation of TDS with ion removal was also observed for fluoride removal using freezing (Yang et al. 2017). Furthermore, the solute impurities and freezing-point depression in polycrystalline ice, formation of complicated and dynamic network of liquid water forms within the solid ice matrix at the boundaries between ice crystal grains (Brox, Skidmore, and Brown 2015).

Table 1. Physicochemical properties of water tested (initial conditions) and melted ice

Parameters	Melted ice obtained from Simulated tap water	Melted ice obtained from frozen deionized water spiked with Cr	Simulated tap water	Deionized Water Spiked with Cr
Conductivity (µS/cm)	46.80	2.60	99.6	2.50
pH	7.40	6.50	7.90	6.40
DO (mg/L)	6.80	6.83	6.81	6.90
Ca^{2+} (mg/L)	28.50		58.60	
Mg^{2+} (mg/L)	14.40		29.30	
Na^{+} (mg/L)	32.40		92.67	
K^{+} (mg/L)	5.59		19.98	
Cr^{+6} (mg/L)	1.75	0.16	5	5
HCO_3^- (mg/)	NM		470	
SO_4^{2-} (mg/L)	NM		60	

Temperature 295.65 K during measurement of pH, conductivity and DO.

NM = Not measured

When evaluating the impact of Cr concentration on its removal from simulated tap water, a nearly equal separation was observed for a wide range of concentrations, up to 100 mg/L Cr(VI). However, at concentrations above 100 mg/L Cr(VI) in the system, the separation percentage decreased (**Fig. 4**). The fact that the freezing process is relatively insensitive to a wide range of Cr concentrations was also reported as an advantage of freeze desalination (Lu and Xu 2010). When the initial Cr(VI) concentration increased afterwards, the solute remains even more concentrated near the ice-water interface, the result became more labile and ice crystal could form dendrites with more advanced ice branches gradually (Yang et.al. 2017).

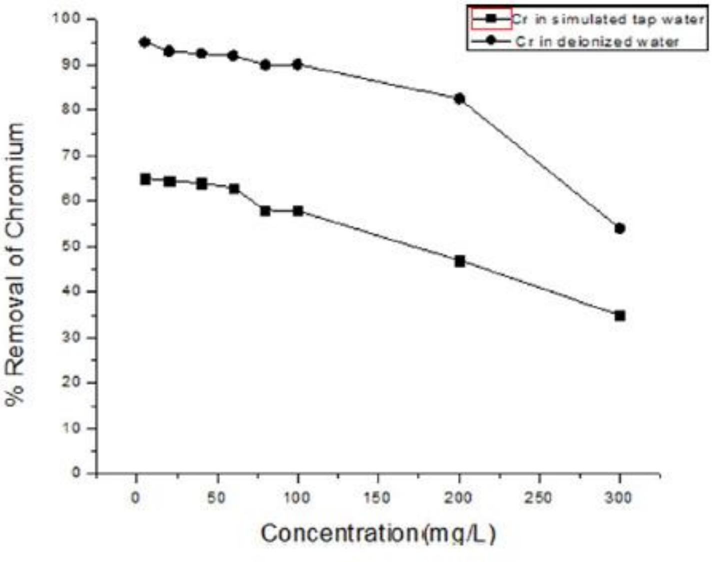

Fig. 4. Effect of initial Cr concentration on Cr removal (% separation) using aqueous solution and simulated tap water when applying freeze desalination at a temperature of 249.15 K (initial volume 250 mL).

The performance of freeze desalination at wide ranges of concentrations was observed in literature for other ions as well (Lorain et al. 2001; Kang et al. 2014). The removal of the ions employed in the experiment for simulation decreased in the order: $K^+ > Na^+ > Mg^{2+} \approx Ca^{2+}$. This was similar to results reported by Kang et al. (Kang et al. 2014), except that they reported the removal of Na^+ being nearly the same as the removal of divalent ions. It seems that the removal efficiency is related to the hydration free energy and the hydrated radius of the ions. Ions in water are found in hydrated forms which can be described as $Mn^+(H_2O)_n$, with n water molecules coordinated with the cation in a geometrically defined hydration shell. Hydration free energy shows the stability of the hydrated ions in reference to their unhydrated counterpart. The magnitude of hydration free energy for the studied ions is provided in the order: $Mg^{2+} > Ca^{2+} > Na^+ > K^+$. Ions having a strong interaction with water molecules are more easily incorporated in the ice phase during freezing. Thus, ions with smaller energy of hydration have less association with water and hence high removal percentage (Hummer et al. 1996; Tansel 2012; Kang et al. 2014).

3.3 Energy efficiency insights of freeze desalination

The cost of desalination technologies depends mainly on the type of physical process (thermal or separation processes e.g., membrane process) involved, but also on other parameters such as plant capacity, feed water quality, pretreatment, plant condition, plant life, and investment assets. As a result, several strategies were proposed and are being implemented to improve the energy efficiency of desalination (Scheumann and Kraume 2009). It is reported that the basic advantage of freeze desalination is the lower energy requirement compared to other thermal processes such as multi-stage flash evaporation (MSF), multiple-effect evaporation/distillation (MED), and vapor compression distillation (VCD). For example, freeze desalination systems require six times lower energy to obtain 1 kg of fresh water compared to MSF. Since compression work is a major cost parameter in freezing, renewable resources may be used to make the technology cost-efficient (Rahman, Ahmed, and Chen 2006; Attia 2010). Recently, researchers are also indicating the possibility of using waste energy application for freeze desalination like Liquefied natural gas (LNG) for energy saving, hence the technology is become promising (Wang and Chung 2012; Chang et al. 2016b). Furthermore, according to Attia (2010), the cost of freeze desalination using an auto-reversed R-22 vapor compression heat pump is 50% lower than most efficient methods reviewed previously (Lara, Noyes, and Holtzapple 2008). Rice and Chau also elaborated the idea of using hydraulic refrigerant in freeze desalination plants, stating that freeze desalination is much more attractive than it has been in the past and should be reconsidered and compared with other means of desalination with regard to energy efficiency and other operating parameters (Rice and Chau 1997). Actual energy consumption using freezers is affected by different factors. For example, it depends on how the appliance is used and where it is located, temperature and others. Table 2 shows the energy consumption and average costs of large scale technologies employed so far.

Table 2. Energy consumption and total average costs of large scale commercial desalination plants

Methods	Total energy kWh/m3	Total average costs	Remark	References
Thermal: Multistage flash evaporation (MSF)	10-16	1.0 $\$/\mathrm{m}^3$	Second largest installed desalting capacity in the world next to RO	(Zhou and Tol 2005)
Thermal: Multiple effect evaporation (ME)	5.5-9	about $\$1.0/\mathrm{m}^3$		(Ghaffour, Missimer, and Amy 2013)
Membrane processes: Reverse osmosis(RO)	6.95	less than $\$0.5/\mathrm{m}^3$	For seawater	(Baayyad et al. 2014; Ettouney 2009)
Electrodialysis (ED)		less than $\$1.0/\mathrm{m}^3$	For seawater	(Zhou and Tol 2005)
		about $\$0.6/\mathrm{m}^3$	For brackish water	
Hybrid method: Coupling freezing and reverse osmosis (RO)	5.17		For seawater	(Baayyad, Hassania, and Bounahmidi 2014)

3.4 Conclusion

Our study confirmed that the freeze separation process seems to have potential for Cr(VI) removal from water, revealing that water rejection was small and relatively efficient, producing 85% (V/V) of melted ice as desalted water. The freezing process revealed that Cr(VI) removal efficiency as high as 97% and 85% for deionized and simulated tap water spiked with 5 mg/L Cr(VI), respectively. However, technical challenges related to washing off the chromium adhered to the ice surface after freezing and separation of ice from water under real conditions outside the laboratory will need special attention when further developing the technology for practical use.

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